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Thermal Isomerizations of 1,1-Dimethyl-2,2-d_2-cyclopropane

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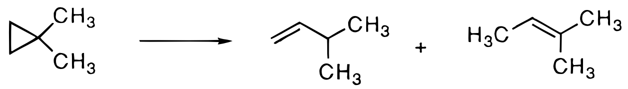
The gas-phase thermal isomerization of 1,1-dimethylcyclopropane at 420 °C gives 3-methyl-1-butene and 2-methyl-2-butene. The mixture of products formed from 1,1-dimethyl-2,2-d_2-cyclopropane is consistent with conventional rationales; neither *tert*-butylcarbene nor isobutylcarbene is involved as a mechanistically significant intermediate. Both kinetic and deuterium labeling evidence suggests that heterogeneous wall-catalyzed processes afford secondary products, including 2-methyl-1-butene.

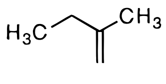
Introduction

The gas-phase thermal isomerization of 1,1-dimethylcyclopropane (**1**) has been investigated in great detail. In a series of classic papers Flowers and Frey characterized the major products formed through homogeneous, unimolecular reactions in "aged" static Pyrex reaction vessels to be 3-methyl-1-butene (**2**) and 2-methyl-2-butene (**3**).[1−3] Kinetic work over the temperature range 447−511 °C with isomerizations of starting material varied between 10% and 60% (to ±2%) led to high-pressure activation parameters for the isomerization, $\log A = 15.05$ and $E_a = (62.6 \pm 0.6)$ kcal/mol. The ratios of products were less accurately determined (to ±5%). The initial **2**/**3** ratio, 1:1.1 (averaged over 300 runs), was pressure and temperature independent. The isomerization rates at 442−481 °C were shown to decrease at lower pressures in highly satisfactory agreement with the requirements set by the Lindemann hypothesis, and they did not go through a maximum at higher pressures.



1 **2** **3**

Other products noted included approximately 1% of 2-methyl-1-butene (**4**) and traces (less than 1%) of some secondary "cracking" compounds such as ethane, ethylene, propane, and propene. Interestingly, 2-methyl-1-butene was not detected in runs at pressures as low as 0.1 mm, and the rates of secondary isomerizations of **2** and **3** proved to be highly pressure dependent.



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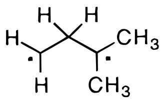

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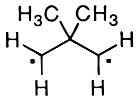
Products **2** and **3** presumably stem from cleavage of the C1−C2 bond in **1** to afford the 1,1-dimethyltrimethylene diradical (**5**) followed by 1,2-hydrogen migration to either C1 or C3. Formation of the minor product **4** might also be derived from this diradical, through transfer of a hydrogen from a methyl group to the terminal methylene.[1]

Work on the chemically activated isomerization of **1** has served as a testing ground for RRKM theory.[4,5]

The isomerization of **1** has been a veritable fixed point in related hydrocarbon thermal rearrangement chemistry shown by other alkyl- and dialkyl-substituted cyclopropanes,[6−8] so long known, well studied, and thoroughly understood that it has not been subjected to experimental or theoretical re-examination in recent decades. One step in this direction is now reported, based on the reactions shown by **1** and by 1,1-dimethyl-2,2-d_2-cyclopropane (**1**-d_2).

Several questions were considered as the present work was initiated. Would substantial deuterium kinetic isotope effects on the overall isomerization or on product distributions be seen? Is **4** really a primary thermal product? Might **1** lead to the 2,2-dimethyltrimethylene diradical (**6**) through cleavage of the C2−C3 bond[9] and then afford product **4** through a methyl migration?[10] Could **1** give rise to isobutylcarbene (**7**) and *tert*-butylcarbene (**8**) intermediates, which through hydrogen or methyl shifts could lead to products **2** and **3**?[11]



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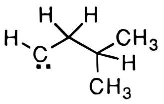

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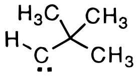

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Experimental Section

All reactions were carried out under a nitrogen or argon atmosphere in flame- or oven-dried glassware. Diglyme was dried over sodium and distilled under nitrogen. *tert*-Butyl alcohol was stored over 4A molecular sieves. Varian Aerograph A90-P3 and Hewlett-Packard 5890 and 5890 Series II instruments and a 3393A integrator were used for preparative and analytical gas chromatography. Bruker instruments (300 and 600 MHz for ^{1}H) were used to obtain NMR spectra.

1,1-Dibromo-2,2-dimethylcyclopropane.[12] A stirred mixture prepared from potassium *tert*-butoxide (8.6 g, 77 mmol), *tert*-butyl alcohol (50 mL), and pentane (50 mL) under argon was cooled in a salt−ice bath; liquid isobutylene (Aldrich Chemical; 12.5 mL, 7.42 g, 132 mmol) was injected, and then bromoform (4.5 mL, 13.0 g, 51 mmol) was added dropwise by syringe. The reaction mixture was stirred and held at 0 °C for 14 h; it was then warmed to room temperature and washed with water (12 × 50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give 8.4 g (71% based on $CHBr_3$) of crude product as a pale-yellow liquid: ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 2 H), 1.62 (s, 6 H).

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1,1-Dimethylcyclopropane.[13] To a stirred suspension of finely divided sodium (2 g) in dry diglyme (50 mL) was added dropwise a mixture of 1,1-dibromo-2,2-dimethylcyclopropane (1 g, 31 mmol) in ethanol (5 g) and water (1 mL). The reaction was exothermic and the temperature was maintained below 70 °C. The product which distilled from the flask was collected in a trap cooled to −78 °C and then purified by distillation, 100 mg (40% yield): ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 6H), 0.20 (s, 4H); MS, *m/z* 70 (M^+, strong), no ion intensity at 68 or 69.

1,1-Dimethyl-2,2-d_2-cyclopropane. 1,1-Dibromo-2,2-dimethylcyclopropane (1 g, 31 mmol) was reduced with sodium in CH_3CH_2OD (5 g; Isotec, min 99 atom % D) and D_2O (1 mL; Aldrich, 99.9 atom % D) following the procedure given above. The deuterium-labeled product was obtained in 40% yield: ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 6 H), 0.20 (s, 2 H); ^{2}H NMR ($CHCl_3$, 5% $CDCl_3$) δ 0.20 (s); MS, *m/z* 72 (M^+, strong), no ion intensity at 70 or 71.

Thermal Reactions. Thermal reactions of **1** and of **1**-d_2 at 420 °C were carried out in a 300 mL Pyrex bulb encased in an aluminum block static reactor.[14] A Bailey Instruments model 253 precision temperature controller and a Hewlett-Packard model 2802A digital thermometer extending into a well in the reactor were employed. The bulb was conditioned before kinetic runs with 100 μL of cyclohexene at 420 °C for 24 h.

Samples of **1** or **1**-d_2 were injected into the evacuated (10^{-2} Torr) reactor through a septum with a gastight syringe; at the end of a thermal reaction all products were transferred under vacuum to a liquid nitrogen cooled U-tube attached to a vacuum line and diluted with *n*-decane.

1,1-Dimethylcyclopropane (**1**) (100 μL) was injected into the kinetic bulb at 420 °C; after 6 h, the product mixture was collected, diluted with decane (100 μL), and separated by preparative gas chromatography on an SE-30 column at 55 °C into three fractions, (**1** + **2**), **4,** and **3**, in order of elution. The identities of these hydrocarbons were established through analytical GC and ^{1}H NMR spectroscopic[15] comparisons with authentic samples.

1,1-Dimethyl-2,2-d_2-cyclopropane (**1**-d_2) (100 μL) was kept for 6 h at 420 °C; the product mixture was collected and diluted with decane (100 μL). Three fractions were collected by preparative GC; they were characterized by ^{1}H and ^{2}H NMR spectroscopy.

1-d_2: ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 6 H), 0.20 (s, 2 H); ^{2}H NMR δ 0.20 (s).

2-d_2: ^{1}H NMR δ 1.00−1.02 (m, 6H), 2.20−2.40 (m, 0.5 H), 4.80−5.00 (m, 1.0 H), 5.75−5.90 (m, 0.5 H); ^{2}H NMR δ 2.20−2.40 (m, 0.49 D), 4.80−5.00 (m, 1.00 D), 5.75−5.90 (m, 0.51 D).

3-d_2: ^{1}H NMR ($CDCl_3$) δ 1.50−1.80 (m, 7.5 H), 5.16−5.30 (m, 0.5 H); ^{2}H NMR δ 1.50−1.80 (m, 1.55 D), 5.16−5.30 (m, 0.45 D).

4-d_2: ^{1}H NMR ($CDCl_3$) δ 1.00−1.10 (m, 1.9 H), 1.70−1.80 (m, 2.9 H), 1.98−2.12 (m, 1.2 H), 4.66−4.74 (m, 2.0 H); ^{2}H NMR δ 1.00−1.10 (m, 1.06 D), 1.70−1.80 (t, 0.14 D, J_{H-D} = 2.25 Hz), 1.98−2.12 (m, 0.75 D), 4.66−4.74 (m, 0.05 D).

Further aspects of the ^{2}H NMR spectra, and of ^{13}C spectra of deuterium-labeled products, are discussed below.

Isomerization Kinetics. Isomerization kinetics were followed using 20 μL samples of neat **1** or **1**-d_2; product mixtures were collected, diluted with decane (50 μL), and analyzed by GC on a J&W GS-Alumina PLOT column at 140 °C with a head pressure of 1.5 psi. Mole percent composition data are given in Tables 1 and 2.

TABLE 1: Mole Percent Compositions of Product Mixtures from 1 at 420 °C

time (h)	**1**	**2**	**3**	**4**
0	100	0	0	0
1.5	81.7	7.6	10.8	0.0
3.5	71.0	11.9	16.7	0.0
7.5	49.0	20.2	29.3	1.5
13	29.6	24.0	42.0	3.0

TABLE 2: Mole Percent Compositions of Product Mixtures from 1-d_2 at 420 °C

time (h)	**1**-d_2	**2**-d_2	**3**-d_2	**4**-d_2
0	100	0	0	0
1.5	82.0	7.2	10.8	0.0
3.5	71.0	12.1	16.9	0.0
7.5	49.0	20.1	29.3	1.6
13	29.9	24.3	42.8	3.0

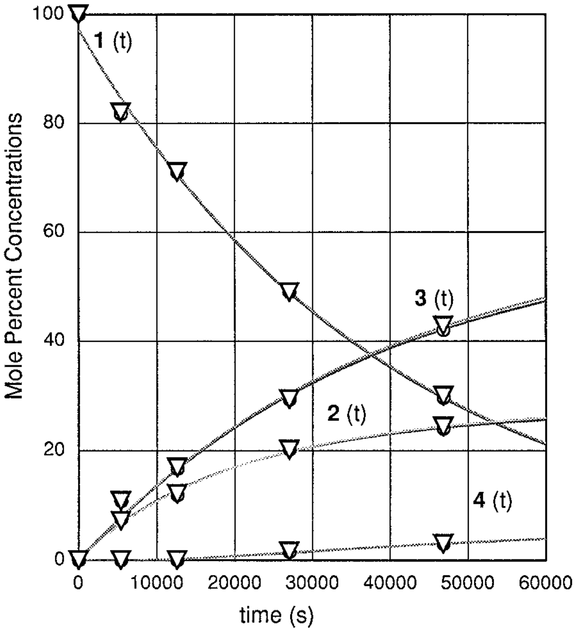


Figure 1. Mole percent concentrations of isomers versus reaction time from thermal isomerizations of **1** (triangles) and **1**-d_2 (circles) at 420 °C.

Results and Discussion

Isomerization Kinetics for 1. A series of gas-phase kinetic runs at 420 °C for up to 13 h showed that **1** isomerized following good first-order kinetics, with an isomerization rate constant $k = 2.55 \times 10^{-5}$ s^{-1}, in fine agreement with the expectation $k = (1.3-3.2) \times 10^{-5}$ s^{-1} based on the reported activation parameters.[1] The relative concentrations of **3** over time were consistent with simple exponential growth, with **3**(t) proportional to $(1 - \exp(-kt))$. The functions **2**(t) and **4**(t), however, were much better fit with two exponential terms.[16] The rate equations appropriate to the minimal kinetic model adopted, **1** to **2** and **3** through parallel first-order reactions and **2** and **4** in equilibrium, led to the theoretical functions[17] used to fit the experimental points, with $k = 2.55 \times 10^{-5}$ s^{-1} and $k' = 6.92 \times 10^{-5}$ s^{-1} (eq 1−4 and Figure 1).

$$\mathbf{1}(t) = 97.2 \exp(-kt) \tag{1}$$

$$\mathbf{2}(t) = 28.6 - 12.9 \exp(-kt) - 15.4 \exp(-k't) \tag{2}$$

$$\mathbf{3}(t) = 60.5 - 60.5 \exp(-kt) \tag{3}$$

$$\mathbf{4}(t) = 6.3 - 11.4 \exp(-kt) + 5.1 \exp(-k't) \tag{4}$$

The kinetically controlled product ratio **2**/**3** calculated from the parameters in eqs 2 and 3 was 1:1.11, in agreement with Flowers and Frey.[3] A sample of **4** heated for 72 h at 420 °C gave a 3:65:32 mixture of **2**/**3**/**4**, proportions nearing the equilibrium ratios one might expect (≈6:70:24) from the standard heats of formation for **1** (−2.0 kcal/mol),[18] **2** (−6.6 kcal/mol),[19] **3** (−9.9 kcal/mol),[20] and **4** (−8.4 kcal/mol).[20] The kinetic behavior depicted in Figure 1 and eqs 1−4 shows that **3**(t) is always present at close to its equilibrium proportion, and possible secondary reactions equilibrating **3** with **2** and **4** may not be very evident in gas chromatographic analyses. For reaction times up to 13 h, the equilibration between **2** and **4** has begun, but it has only begun; **2**(t) remains larger than **4**(t), while at equilibrium **2**/**4** is about 1:4.

Isomerization Kinetics for 1-d_2. Kinetic runs with **1**-d_2 at 420 °C for times up to 13 h gave very similar relative mole percent versus time profiles. The data were fit using the same theoretical functions used to model the reactions of **1**, as summarized in eq 5−8; the exponential constants were found to be $m = 2.53 \times 10^{-5}\ \mathrm{s}^{-1}$ and $m' = 6.92 \times 10^{-5}\ \mathrm{s}^{-1}$. The R^2 regression coefficients for the data fits expressed in eq 1−8 ranged from 0.987 to 0.998.

$$\mathbf{1}\text{-}d_2(t) = 97.2 \exp(-mt) \tag{5}$$

$$\mathbf{2}\text{-}d_2(t) = 29.4 - 14.4 \exp(-mt) - 14.8 \exp(-m't) \tag{6}$$

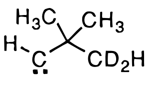
$$\mathbf{3}\text{-}d_2(t) = 61.4 - 61.4 \exp(-mt) \tag{7}$$

$$\mathbf{4}\text{-}d_2(t) = 6.3 - 11.2 \exp(-mt) + 4.9 \exp(-m't) \tag{8}$$

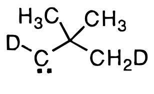
The data plots included in Figure 1 emphasize how little impact the deuterium labels have on overall kinetic behavior. The initial ratio of **2**-d_2/**3**-d_2 products calculated from eqs 6 and 7 was 1:1.12, nearly identical with the 1:1.11 ratio found for **2**/**3**. The calculated rate constant ratios k/m and k'/m' are 1.01 and 1.00. These ratios, related to some combination of equilibrium (to diradicals or other intermediates) and primary and secondary deuterium kinetic isotope effects provide no striking mechanistic insights. Yet the comparative kinetic data (Figure 1) do provide an important assurance; the **1**-d_2 sample contains no trace of a catalytically significant impurity, and thus the distributions of deuterium labels in products **2**-d_2, **3**-d_2, and **4**-d_2 will be indicative of whatever paths may be followed in unlabeled 1,1-dimethylcyclopropane and should be consistent with kinetically derivable inferences.

Deuterium Labeled Products. A thermal reaction of **1**-d_2 for 6 h at 420 °C gave a product mixture which was separated and purified by preparative gas chromatography.

1-d_2. The deuterium NMR spectrum of recovered starting material showed only one absorption, for cyclopropyl CD_2 at δ 0.20. There was no detectable absorption intensity at δ 1.03 for deuterium in a methyl group, which effectively excludes any mechanistically significant formation of *tert*-butylcarbene as an intermediate leading to **3**. Were *tert*-butylcarbene involved, the deuterium-labeled analogues derived from **1**-d_2 would have been **8**-d_2-a and **8**-d_2-b, both of which would have given some 1,1-dimethylcyclopropane with deuterium in a methyl group[21,22] as well as deuterium labeled versions of **3**.



8-d_2-a



8-d_2-b

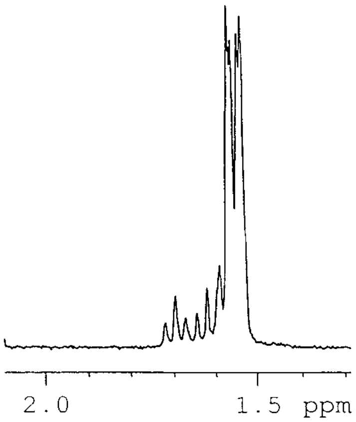
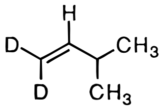
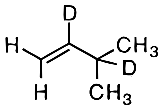


Figure 2. Methyl ^{2}H NMR absorptions for **3**-d_2.

2-d_2. The ^{2}H NMR spectrum of the labeled 3-methyl-1-butene formed was consistent with **1**-d_2 giving a 1:1 mixture of **2**-d_2-a and **2**-d_2-b. The cis and trans vicinal H−D coupling constants (1.5 and 2.6 Hz) apparent at δ 5.00 and 4.90 for **2**-d_2-a and at δ 5.80 for **2**-d_2-b correspond with expectations; the vinyl $J^3_{\mathrm{H-H}}$ values for propene are 10.0 and 16.8 Hz, which when divided by 6.51, the ratio of magnetogyric ratios $\gamma_{\mathrm{H}}/\gamma_{\mathrm{D}}$,[23,24] give 1.5 and 2.6 Hz. No signal intensity was detected at δ 1.03 for a deuterium in a methyl group.

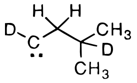


2-d_2-a

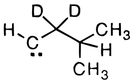


2-d_2-b

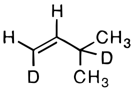
The formation of **2**-d_2-a and **2**-d_2-b from **1**-d_2, rather than isotopomers **2**-d_2-c to **2**-d_2-f, rules out any significant role for carbene intermediates **7**-d_2-a and **7**-d_2-b.



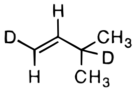
7-d_2-a



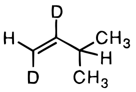
7-d_2-b



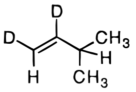
2-d_2-c



2-d_2-d



2-d_2-e

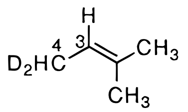


2-d_2-f

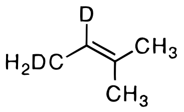
The ^{2}H NMR results also suggest that **2**-d_2 is not being formed to any substantial extent over the first 6 h of reaction from other isomers; secondary reactions of **3**-d_2 or **4**-d_2 to form **2**-d_2 play no important role. This inference is of course consistent with thermochemical considerations. A sample of **2**-d_2 obtained from a 19 h thermal reaction had a similar ^{2}H NMR spectrum, but there were noticeable differences: the relative absorption intensities for deuterium at C1, C2, and C3 were 1.71:1.00: 0.88. At such long reaction times there may be redispositions of deuterium labels through secondary reactions and perhaps some loss of deuterium.

3-d_2. The ^{2}H NMR spectrum of **3**-d_2 derived from **1**-d_2 showed absorptions at δ 5.2 and in the 1.5−1.7 methyl region with relative intensities of 0.45:1.55. The strongest methyl region component was centered at δ 1.55, a four-line pattern for the C4−CHD_2 unit (Figure 2), with geminal and vicinal $J_{\mathrm{H-D}}$ couplings of 3.0 and 0.8 Hz. Thus, **3**-d_2-a is formed, and **3**-d_2-b seemed the most plausible component responsible for the vinyl

^{2}H NMR signal. Closer examination of the spectra, however, revealed a slightly more complex mixture.



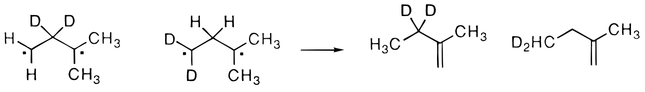
3-d_2-a



3-d_2-b

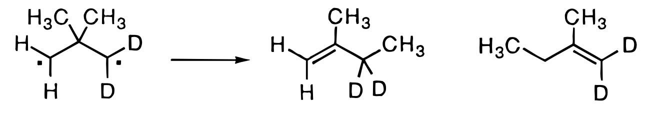
Small amounts of deuterium label were found in the other two methyl groups, as CH_2D at δ 1.6 and 1.7 (Figure 2). Through ^{13}C {^{1}H} NMR spectroscopy, several deuterium labeled versions of the C3−C4 moiety were detected. The ^{13}C chemical shifts for C3 and C4 are reported as δ 118.45 and 13.41, respectively.[15] Thanks to the upfield chemical shift perturbations associated with deuterium substitution[25] and distinctive spin−spin coupling patterns for carbons bonded to zero, one, or two deuterium atoms, $H-C-CH_3$, $H-C-CH_2D$, and $H-C-CD_2H$ substructures were evident as singlets at δ 118.42, 118.38, and 118.35, and $D-C-CH_3$ and $D-C-CH_2D$ were seen as triplets at δ 118.085 and 118.049, with $J_{\mathrm{C-D}} = 23.2 \pm 0.2$ Hz. These variations were confirmed in the absorptions for the C4 methyl group alternatives (Figure 3), showing singlets for $H-C-CH_3$ and $D-C-CH_3$ at δ 13.38 and 13.26, a triplet for $D-C-CH_2D$ at 12.99 ($J_{\mathrm{C-D}}$ 19.2 $\pm$ 0.1 Hz), and a quintet for $H-C-CD_2H$ at 12.84 ($J_{\mathrm{C-D}}$ 19.2 $\pm$ 0.1 Hz). Although **3**-d_2-a and **3**-d_2-b may be considered major components of the 2-methyl-2-butene formed from **1**-d_2, the presence of other isotopomers suggests that indirect, secondary reactions contribute as well.

4-d_2. Expectations for 2-methyl-1-butene-d_2 products derived directly from **1**-d_2 through the two most plausible standard unimolecular thermal mechanisms are easily outlined. If reaction were to take place through intermediates **5**-d_2-a and **5**-d_2-b and migration of hydrogen from a methyl group, then the product would be a mixture of **4**-d_2-a and **4**-d_2-b.



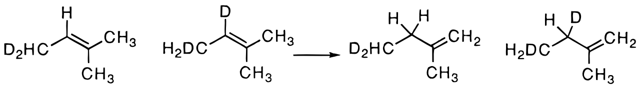
5-d_2-a 5-d_2-b 4-d_2-a 4-d_2-b

If the C2−C3 of **1**-d_2 were to cleave to form **6**-d_2 followed by methyl migration, the product would be a mixture of **4**-d_2-a and **4**-d_2-c.



6-d_2 **4-d_2-a** **4-d_2-c**

But expectations based on the kinetic evidence would be of a different nature; one would need to consider possible mechanisms for secondary isomerizations from the isotopomers of **2**-d_2 and **3**-d_2 in the product mixture. For instance, if products were derived from **3**-d_2-a and **3**-d_2-b through protonation at C2, followed by deprotonation, one would expect formation of **4**-d_2-b and **4**-d_2-d.



3-d_2-a **3-d_2-b** **4-d_2-b** **4-d_2-d**

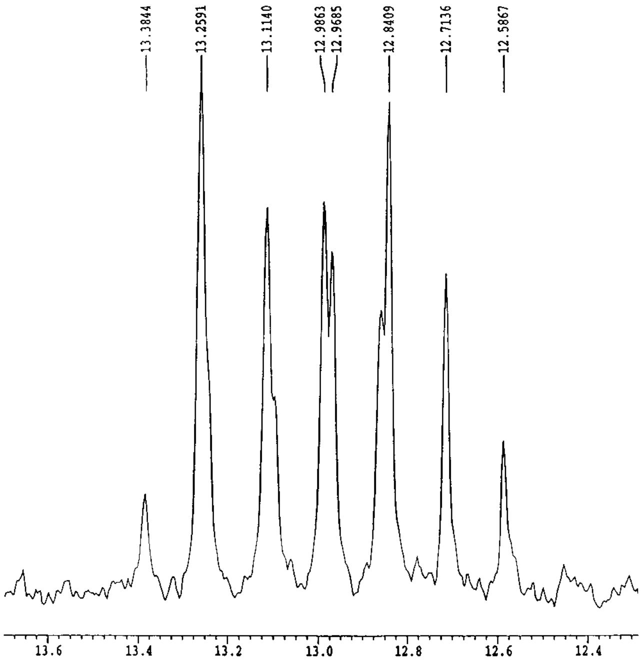
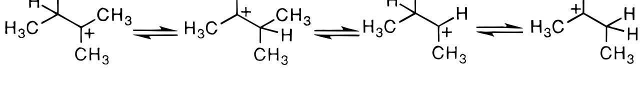


Figure 3. Absorptions for C4-methyl for various **3**-d_2 isotopomers in a ^{13}C {^{1}H} NMR spectrum at 150.856 MHz.

The experimental ^{2}H NMR spectrum for **4**-d_2 from a 6 h reaction mixture showed deuterium at every position, with relative intensities 0.05 (C1), 0.14 (C2-methyl), 0.75 (C3), and 1.07 (C4). The intensity ratios for **4**-d_2 from a 19 h reaction mixture were 0.09:0.17:0.60:1.14, quite similar and yet not identical. The **4**-d_2 product is a complex mixture of isotopomers, formed presumably from the several versions of **2**-d_2 and **3**-d_2 present in reaction mixtures. The ^{13}C{^{1}H} NMR spectrum of the 6 h **4**-d_2 mixture provides further evidence for extensive scrambling. For instance the C4 absorptions reflect contributions from CH_3CH_2-, CH_3CHD-, and CH_3CD_2- (singlets at δ 12.27, 12.19, and 12.11), CH_2DCH_2- and CH_2DCHD- (triplets at 11.98 and 11.90), and CD_2HCH_2- (quintet at 11.69), with all triplets and the quintet having $J_{\mathrm{C-D}}$ 19.4 Hz. The deuterium isotope effects on ^{13}C chemical shifts are very much in line with expectations.[25]

Homogeneous and Surfaced-Catalyzed Reactions. The structural isomerizations leading to equilibration of alkenes **2**, **3**, and **4**, as well as the observed distributions of deuterium labels in alkene products, point to surface-catalyzed reactions. Even after thorough "aging" or "conditioning" of a kinetic bulb, there may be Si−O−H groups on the surface that can trigger cationic reactions. In the present case, one can well imagine proton transfers from surface to alkenes, initiating equilibrations of 2-methyl-2-butyl cations (*tert*-amyl cations or dimethylethylcarbonium ions) and 3-methyl-2-butyl cations. These isomerizations through both hydrogen and methyl shifts have been documented by isotopic labeling experiments[26,27] and by NMR spectroscopic studies.[28]



Each of these cationic structures could be formed from, or could lead to, two of the alkenes involved; the 3-methyl-2-butyl cation is related to **2** and **3**, and the 2-methyl-2-butyl cation to **3** and **4**. Protonations of alkenes, carbocation isomerizations, and deprotonations could lead to equilibrations among the three alkenes and an approach to the thermodynamically defined equilibrium mixture, to scramblings of deuterium labels, and to some loss of label, all processes one may infer from the experimental findings.

Conclusions

The kinetic indications and the deuterium labeling results provide persuasive grounds for considering the isomerization of 1,1-dimethylcyclopropane (**1**) to the isomeric alkenes 3-methyl-1-butene (**2**) and 2-methyl-2-butene (**3**) at 420 °C as reactions that proceed through parallel first-order processes. There are no significant net deuterium kinetic isotope effects distinguishing the thermal isomerizations of **1** and **1**-d_2. Alkylcarbene intermediates **7** and **8** are not involved. The traditional mechanistic formulations based on hydrogen migrations from the 1,1-dimethyltrimethylene diradical (**5**) appear quite adequate. 2-Methyl-1-butene (**4**) is not a primary product; it is formed only through secondary surface-catalyzed isomerizations that equilibrate **2**, **3**, and **4**. These secondary reactions introduce kinetic and deuterium labeling complexities that might well have interfered with the objectives of some labeling experiments, but they did not impinge on the tests for the intervention of alkylcarbene intermediates now being reported.

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